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# **Passive Sampling for Indoor and Outdoor Exposures to Chlorpyrifos, Azinphos-Methyl, and Oxygen Analogs in a Rural Agricultural Community**

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**Short Running Title:** Measurement of pesticides and analogs in a rural community.

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**Abstract:**

**Background:** Recent studies have highlighted the increased potency of oxygen analogs of organophosphorus pesticides. These pesticides and oxygen analogs have previously been identified in the atmosphere following spray applications in California and Washington states.

**Objectives:** In 2011, we used two passive sampling methods to measure organophosphorus pesticides chlorpyrifos, azinphos-methyl, and their oxygen analogs at 14 farmworker and 9 non-farmworker households in an agricultural region of central Washington State.

**Methods:** The passive methods included: a) polyurethane foam passive air samplers deployed outdoors and indoors; and b) polypropylene deposition plates deployed indoors. We collected cumulative monthly samples during the pesticide application seasons and during the winter season as a control.

**Results:** Monthly outdoor air concentrations ranged from 9.2 - 199 ng/m<sup>3</sup> for chlorpyrifos, 0.03 - 20 ng/m<sup>3</sup> for chlorpyrifos-oxon, < LOD - 7.3 ng/m<sup>3</sup> for azinphos-methyl, and < LOD - 0.8 ng/m<sup>3</sup> for azinphos-methyl-oxon. Samples from proximal households ( $\leq 250$  m) had significantly higher outdoor air concentrations of chlorpyrifos, chlorpyrifos-oxon, and azinphos-methyl than samples from non-proximal households ( $p \leq 0.02$ ). Overall, indoor air concentrations were lower than outdoors. For example, all outdoor air samples for chlorpyrifos and 97% of samples for azinphos-methyl were above limits of detection (LOD). Indoors, only 78% of air samples for chlorpyrifos and 35% of samples for azinphos-methyl were  $> LOD$ . Samples from farmworker households had higher indoor air concentrations of both pesticides than samples from non-farmworker households. Mean indoor/outdoor air concentration ratios for chlorpyrifos and azinphos-methyl were 0.17 and 0.44, respectively.

**Conclusions:** We identified higher levels in air and on surfaces at both proximal and farmworker households. Our findings further confirm the presence of pesticides and their oxygen analogs in air, and highlight their potential for infiltration of indoor living environments.

## Introduction

### *Organophosphorus pesticides and oxygen analogs*

In the Yakima Valley region of Washington State, there are over a thousand orchards (e.g., apples, pears, cherries) covering more than 100,000 acres. Washington is the lead producer of apples and cherries in the United States, and 10-12 billion apples are picked each year (USDA 2009) (See Figure 1 for a map of the region). The region is also home to many farmworker families and more than half of the population is Hispanic/Latino (US CENSUS 2010). Most of this population is involved in tree fruit production-- harvesting, pruning, thinning, and application of agricultural chemicals (Thompson et al. 2008). In 2011, chlorpyrifos (CPF) and azinphos-methyl (AZM) were some of the most commonly applied organophosphorus (OP) pesticides in tree fruit and vegetable production (Baker and Stone 2015). Both pesticides are often applied in aerosolized form to tree fruits using a large sprayer attached to a tractor. In 2012, the United States Environmental Protection Agency (US EPA) banned the use of AZM in apple production. Prior to the ban, when this study was conducted, AZM and CPF were commonly sprayed with application rates averaging 0.5 kg/acre and 1 kg/acre active ingredient, respectively (USDA 2002, 2009).

The use of OP pesticides in Yakima Valley has long been a health concern of local residents due to potential human exposures resulting from off target volatilization and drift. In 2008, the Washington state government funded a study to examine off-target movement of OP pesticides and potential risk to bystanders (Fenske et al. 2009). In the 2009 study, CPF, AZM, and their oxygen analogs were identified in the outdoor air of the surrounding agricultural communities, indicating direct atmospheric transformation. Other studies have also reported these compounds in air (Armstrong et al. 2013b; CARB 1998; CDPR 2006, 2009).

Toxicology studies have focused on the relative potency of combined OP pesticides and their oxygen analogs in animal models (Costa et al. 2005), and acknowledge transformation to the oxygen analog *in vivo* as a metabolic product through breakdown mechanisms involving cytochrome p450 enzymes. Chlorpyrifos-oxon (CPF-O) poses a special risk for genetically susceptible individuals who have lower levels of the paraoxonase [PON-1(-/-)] enzyme (Shih et al. 1998), and children may be susceptible to the CPF-O due to their differences in metabolic functioning during development (Barr et al. 2004; Costa et al. 2005). Therefore, it is important to consider the presence of oxygen analogs in the air when measuring human exposure.

In several studies over a decade ago we found that levels of OP pesticide metabolites in the urine of farm worker children were significantly higher than levels in the urine of non-farm worker children in the same region (Loewenherz et al. 1997; Lu et al. 2000), and later confirmed these relatively high levels by comparison with national biomonitoring data (Fenske et al. 2005). We also found that pesticide levels in household dust (including AZM and CPF) were higher in farm worker homes than in non-farmworker homes in the same region (Lu et al. 2000; Fenske et al. 2002)

CPF and AZM are both semivolatile compounds and they exist as both vapor and particle-bound forms in air. This phase-partitioning is highly dependent on a combination of pesticide application timing and meteorological factors (Howard 1991). Both compounds can persist for days to weeks outdoors, and for several months indoors (Lewis 2005, Wauchope et al. 1992). There is very little scientific data regarding the long term atmospheric transport of CPF, AZM, CPF-O, and AZM-O and even less is known about their ability to infiltrate indoor environments.

### ***Passive sampling for pesticides***

To date, many epidemiology studies have focused on short and long term human health outcomes associated with OP pesticides, although very few have incorporated long term air and surface exposure measurements for OP pesticides and oxygen analogs due to the high costs and invasive procedures associated with residential sampling. The oxygen analogs (CPF-O and AZM-O) are relatively new phenomena, and, to our knowledge, no studies have measured them in residences.

Although active air sampling is useful for examining daily fluctuations or collecting a personal sample over the course of a work shift, it involves frequent collection of sampling media, use of electricity, and requires space for the sampling pumps. In a previous study (Armstrong et al. 2013a), we identified artificial transformation from CPF to CPF-O during active air sampling with OVS/XAD-2 tubes (NIOSH 1994) in a controlled laboratory environment. In response, we developed a polyurethane foam passive air sampling method (PUF-PAS) that was able to sample for OP pesticides and their oxygen analogs at rates similar to active air sampling at 2 liters per minute (Armstrong et al. 2014a). CPF and AZM are both suitable for passive air sampling because they have ideal chemical properties, including octanol-air partition coefficients ( $\log K_{oa}$  values) that fall somewhere between polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) (See Table 1).

Another common indoor passive sampling method involves deposition plates to collect settled particulate. Since the deposition method collects larger diameter particles (as opposed to gases), it is a useful measure of particle-bound phase and dust settling. Deposition plates for indoor OP pesticides have been used in previous studies using polyethylene, chromatography

paper, and double-layer gauze pads backed by aluminum foil (Keenan et al. 2010; Lu et al. 1998).

Our overall aim of this study was to use passive sampling methodologies to measure airborne and surface deposition levels of CPF, AZM, CPF-O, and AZM-O outside and inside of households in a rural agricultural region. Our secondary aim was to compare the levels between proximal/non-proximal and farmworker/non-farmworker households to determine if certain groups were at higher risk of exposure.

## Study Methods

### *Sampling Plan*

We conducted the residential sampling during three seasons in 2011: a) the spring pre-thinning season for CPF and CPF-O, b) the summer thinning season for AZM and AZM-O, and c) winter dormant season for CPF, CPF-O, AZM, and AZM-O (see Figure 2 for timeline). The pre-thinning application, thinning application, and winter dormant seasons were defined using CPF and AZM product information from the Decision Aid System (Washington State Pest Management Resource Service, 2011), which uses meteorological and entomology data to predict optimal pesticide application times for tree fruit producers. In addition, we contacted local Washington State agricultural extension agents to inform us about field activity.

Twenty-three sampling locations were selected *a priori* to be equally grouped as proximal and ( $\leq 250$  m of any nearest tree fruit field) and non-proximal ( $> 250$  m). Of these, 20 locations were recruited from households enrolled with the *Para Niños Saludables* project. This is a community based research project led by researchers at the Fred Hutchinson Cancer Research Center involving a cohort of 60 farmworker and 40 non-farmworker families. We

defined farmworker households as having one or more current farmworkers (temporary or full time), and non-farmworker households as having no farmworkers living in the household (employment status was obtained from 2011 *Para Niños Saludables* household survey). Details about the project and population have been previously reported by Thompson et al. (2008). Overall, there were 6 proximal farmworker, 2 proximal non-farmworker, 7 non-proximal farmworker, and 5 non-proximal non-farmworker households (see Supplemental Material, Table S1).

The 3 remaining sampling locations were outdoor community air monitoring sites (managed by the Yakama Nation tribal Environment Protection Program) within 100 meters of the nearest *Para Niños Saludables* residence. These community locations were required during the study to support replicate sampling and side-by-side comparisons with the active air sampling methods for quality assurance purposes. In addition, for data analysis, at these locations the outdoor measurements were used as surrogates for the nearest household. We used proximity and farmworker employment data from the nearest household, and checked to make sure surrogate community locations and participant residences were equidistant from tree fruit fields. One of the community sites was rurally located near a proximal farmworker household. The other two community sites were urban, near non-proximal non-farmworker households.

We plotted all locations in ArcGIS 10.0 (ERSI, Redlands, CA) using GPS coordinates collected with a GPS Map 60CS handheld unit (Garmin, Inc. Olathe, KS). We identified tree fruit fields using a Cropland Data Layer from USDA CropScape. The Cropland Data Layer is a geo-referenced, crop-specific land cover data layer created annually using satellite imagery and extensive agricultural ground cover (USDA-NASS 2012). We checked to make sure surrogate community locations and participant residences were equidistant from tree fruit fields. Since

such a large portion of the rural community was involved in agriculture, it was challenging to identify non-farmworker households that were also proximal (only 2 households were recruited).

We collected a total of 66 outdoor air samples (CPF and CPF-O,  $n = 36$ ; AZM and AZM-O,  $n = 30$ ), and 53 indoor air and surface deposition samples (CPF and CPF-O,  $n = 27$ ; AZM and AZM-O,  $n = 26$ ) during the application seasons. These numbers include duplicate and triplicate samples deployed in the same location at the same time for quality control purposes (see Supplemental Material, Table S1 for description of replicate samples). We deployed 7 outdoor air samples and 7 indoor air and surface deposition samples at six locations during the winter dormant season as a control. These winter locations were chosen for optimal geospatial distribution across the region.

This study followed protocols approved by the Fred Hutchinson Cancer Research Center Institutional Review Board. Written informed consent (in Spanish or English) was obtained for all households in the study. A field industrial hygienist scheduled a meeting with the *promotora* and the household members to set up the samplers. Outdoors, we located the PUF-PAS away from children's play areas, buffers ( $\geq 8$  m from trees and buildings), livestock, and other high foot traffic areas. Indoors, we placed the PUF-PAS and deposition plates in the living room or kitchen to capture an area of the house where family members spend a large amount of time. This location was placed  $\geq 1$  m height on a shelf or desk to minimize interference or contact with other surfaces (e.g., walls, windows, doors). Monthly sampling periods ranged from 24 to 32 days. At each household, outdoor and indoor samples were deployed and collected on the same day. During the time of collection, we obtained qualitative participant feedback about the passive samplers.

## ***Sampling Materials***

The PUF-PAS device uses properties of atmospheric diffusion to collect contaminants without the use of a pump and sampling rate is controlled by diffusivity (Hourani and Underhill 1988; Shoeib and Harner 2002). The PUF-PAS method for measurement of OP pesticides and oxygen analogs was previously tested in both laboratory and field environments by Armstrong et al. (2014a) using depuration compounds and side-by-side comparisons with more traditional active sampling methods (US EPA 1999). We derived average air concentration ( $C_{\text{air}}$ , ng/m<sup>3</sup>) from the sampling rate ( $R_{\text{PUF-PAS}}$ , m<sup>3</sup>/day) and the mass of pesticide on the matrix ( $M_{\text{pas}}$ , ng), where  $t$  = time in days (*Eq. 1*):

$$C_{\text{air}} = M_{\text{pas}} / (R_{\text{PUF-PAS}} * t) \quad (\text{Eq. 1})$$

Prior to deployment, we spiked each outdoor PUF-PAS with depuration compounds [210 ng of CPF-methyl-D<sub>6</sub> (99%, 100 µg/mL in acetonitrile, EQ Laboratories, Atlanta GA) and 450 ng of AZ-ethyl-D<sub>10</sub> (98.5%, 1000 µg/mL in toluene, EQ Laboratories)] with a 50 µL Hamilton positive displacement syringe. Depuration compounds were not used indoors to ensure safety of residents. We calculated outdoor sampling rates, or  $R_{\text{PUF-PAS}}$ , using the loss of depuration compounds from the PUF matrix and by calibration with side-by-side active air sampling (AAS). All procedures and calculation of sampling rates have been described by Armstrong et al. (2014a).

Outdoors, we placed the PUF-PAS disk (Tisch, Environmental, 14 cm in diameter, 1.3 cm thick, surface area 370 cm<sup>2</sup>) in a stainless steel, domed chamber (22 cm diameter) to protect from wind, precipitation, and sunlight (Shoeib and Harner 2002; Schuster et al. 2012; Tuduri et al. 2006). Air was allowed to flow over the PUF disks through a 1.5 cm gap between chamber encasements. The sampling housing was hooked to a steel sampling mast at 1.5 m height. After

collection, the PUF sample media was sealed in a glass petri dish, and stored placed in a -20°C freezer.

Indoors, the shape and surface area of the PUF-PAS was cylindrical (7 x 3 cm diameter, 74 cm<sup>2</sup> surface area), and similar to the ‘mini-PUF’ introduced by Bohlin et al. (2010). We hung cylinder from a 22 cm tall free-standing hook. Next to the indoor PUF-PAS, a small surface deposition plate consisting of a Petri dish (6 cm diameter, 89000-300 VWR) lined with a polypropylene (PP) filter (5 µm pore, 17.3 cm<sup>2</sup> surface area, Whatman) collected deposited particulate. A temperature logger (LogTag TRIX-8) was placed near both passive sampling devices. After collection we wrapped indoor PUF-PAS cylinders in aluminum foil and stored them in zipper-sealed bags, covered and sealed deposition plates, and stored both sample types similarly to outdoor samples. Indoor air concentrations ( $C_{\text{air}}$ , ng/m<sup>3</sup>) were derived using the same calculation (*Eq. 1*) as for outdoors. Since depuration compounds were not used indoors, indoor sampling rates ( $R_{\text{PUF-PAS}}$ , m<sup>3</sup>/day) were estimated using the  $K_A$  (air-side mass transfer coefficient) and the surface area ( $S_{\text{area}}$ ) of the indoor PUF cylinder (74 cm<sup>2</sup>) (*Eq. 2*). We determined  $K_A$  from the average loss of depuration compounds in previous laboratory tests at 25°C (Armstrong et al. 2014a).  $K_A$  was adjusted for average indoor temperatures recorded by the indoor temperature logger. The calculation, below, has also been described by Shoeib and Harner (2002) (*Eq. 2*):

$$\text{Indoor } R_{\text{PUF-PAS}} = K_A \times S_{\text{area}} \quad (\text{Eq. 2})$$

For the surface deposition samples, we divided the mass of pesticide ( $M_{\text{pp}}$ ) by the surface area ( $S_{\text{area}}$ ) to obtain a mass loading ( $S_{\text{load}}$ , ng/cm<sup>2</sup>) (Butte and Heinzow 2002) (*Eq. 3*):

$$S_{\text{load}} = M_{\text{pp}} / (S_{\text{area}}) \quad (\text{Eq. 3})$$

### **Chemical Analysis**

Preparation and storage of PUF-PAS matrices followed similar procedures in past literature (Bohlin et al. 2010, Shoeib and Harner 2002). We rinsed petri dishes and aluminum foil with solvent during extraction. PUF-PAS and PP filter matrices were sonicated for 1.5 hours at room temperature (20-23°C) in 10-50 mL acetonitrile solution containing stable-isotope labeled internal standards and then evaporated to 1.5 mL. Large particulate was filtered with a PTFE syringe filter (13 mm, 0.2  $\mu\text{m}$  porosity). Sample analysis was conducted using the liquid chromatography tandem mass spectrometry (LC-MS/MS) method with internal standards (Armstrong et al. 2014a, 2014b). Instrument limits of detection (LOD) were 1 ng/sample for CPF and CPF-O, and 1 ng/sample AZM, and 5 ng/sample for AZM-O. The instrument LOD for all depuration compounds was 1 ng/sample. After accounting for the volume of PUF-PAS and surface area of deposition plates, this corresponded to PUF-PAS method Limit of Quantification (LOQ) ranging from 0.01 - 0.02  $\text{ng}/\text{m}^3$  for CPF/CPF-O and 0.02 - 0.03  $\text{ng}/\text{m}^3$  for AZM/AZM-O; and a surface deposition plate method LOQ of 0.03  $\text{ng}/\text{cm}^2$  for CPF/CPF-O and 0.17  $\text{ng}/\text{cm}^2$  for AZM/AZM-O.

Coefficients of variation (CV) were  $\leq 19\%$  for CPF,  $\leq 9\%$  for CPF-O,  $\leq 37\%$  for AZM, and  $\leq 10\%$  for AZM-O in outdoor air samples; and  $\leq 6\%$  for CPF indoor air samples. For the surface deposition plates, CVs were  $\leq 15\%$  for CPF and all replicate samples for AZM were below the LOD. We were unable to calculate CVs for AZM, CPF-O, and AZM-O from indoor air samples and surface deposition plates because replicate samples were  $< \text{LOD}$ . All field blanks were below the LOD for CPF, CPF-O, AZM, and AZM-O. Storage stability and spike fortification recovery results were 80 to 120 % for all measured compounds.

### ***Data Analysis***

For air samples below the LOD, we assigned a substitute value for  $M_{pas}$  and  $M_{pp}$  by taking  $LOD/(\sqrt{2})$  and divided by the effective air sampling volume (*Eq. 1 and 2*), or surface area (*Eq. 3*), respectively. We calculated the mean, standard deviation, and range for outdoor and indoor air concentrations ( $ng/m^3$ ) and indoor surface deposition ( $ng/m^2$ ) among household types (i.e., proximal farmworker, proximal non-farmworker, non-proximal farmworker, and non-proximal non-farmworker). We compared group results using a 2-way non-parametric Friedman test ( $\alpha = 0.10$ ), which is similar to a parametric repeated measure ANOVA (Zimmerman et al. 1993). Next, we compared outdoor and indoor air concentrations and indoor surface deposition in proximal vs. non-proximal and farmworker vs. non-farmworker variables using a non-parametric Kruskal-Wallis one way ANOVA test ( $\alpha = 0.05$ ). Replicate samples were included in these calculations.

Since both outdoor and indoor air samples were collected simultaneously, we calculated indoor/outdoor mean ratios for each household by dividing the indoor air concentration by the outdoor air concentration (the mean of replicate samples was used when necessary). We then calculated the mean of these ratios by household type. A ratio greater than 1 indicates higher indoor pesticide concentrations, whereas a ratio less than 1 indicates higher outdoor pesticide concentrations. We compared indoor/outdoor mean ratios in proximal vs. non-proximal and farmworker vs. non-farmworker households using a non-parametric Kruskal-Wallis one way ANOVA test ( $\alpha = 0.05$ ).

Finally, we calculated the Spearman's correlation coefficient ( $R_s$ ) between air concentrations and surface deposition indoors. Since replicate sampling can influence correlation results, the mean of replicate samples was used for this calculation. All statistical calculations were performed in STATA 11.2 (College Station, TX). We did not compare group

results of outdoor and indoor air concentrations or indoor surface deposition for the winter samples due limitations of small sample size. We deployed samples in the winter to primarily test for presence of OP pesticides during a dormant season.

## Results

### *Outdoor Air Concentrations*

We present the results of outdoor air concentrations by household type in Table 2. All air samples yielded detectable CPF and CPF-O. During the spring, cumulative residential air concentrations of CPF ranged from 9.2 to 199 ng/m<sup>3</sup>, and concentrations of CPF-O ranged from 0.03 to 20 ng/m<sup>3</sup>. We identified the highest levels of CPF (3 of 36 samples > 100 ng/m<sup>3</sup>) at proximal farmworker households within 100 m of apple, peach, corn, or wheat fields. We identified the highest levels of CPF-O (3 of 36 samples > 13 ng/m<sup>3</sup>) at both proximal farmworker and proximal non-farmworker households within 100 m of apple, peach, corn, or wheat fields.

Although 29 of 30 (97%) air samples yielded detectable AZM, only 10 of 30 (33%) samples had detectable AZM-O. During the summer, cumulative air concentrations of AZM and AZM-O were lower than for CPF and CPF-O. Air concentrations of AZM ranged from < LOD to 7.3 ng/m<sup>3</sup> and AZM-O ranged from < LOD to 0.8 ng/m<sup>3</sup>. We identified the highest levels of AZM (3 of 30 samples > 4 ng/m<sup>3</sup>) and AZM-O (3 of 30 samples > 0.3 ng/m<sup>3</sup>) at proximal farmworker households within 200 m of apple, peach, and cherry fields.

There were significant differences in outdoor air concentrations of CPF, CPF-O, and AZM between proximal-farmworker, proximal non-farmworker, non-proximal farmworker, and non-proximal non-farmworker households (Table 2, 2-way Friedman's test,  $p < 0.10$ ). Proximal households had higher mean outdoor air concentrations CPF, CPF-O, and AZM than non-

proximal households; and farmworker households also had significantly higher mean outdoor air concentrations CPF and CPF-O than non-farmworker households (Table 3, Kruskal Wallis test,  $p < 0.05$ ).

### ***Indoor Air Concentrations***

We also present the results of indoor air concentrations by household type in Table 2. Overall, cumulative indoor air concentrations were lower than outdoor concentrations. For example, 21 of 27 (78%) of indoor air samples yielded detectable levels of CPF, and only 7 of 27 (26%) had detectable levels of CPF-O. During the spring, indoor air concentrations of CPF ranged from  $< \text{LOD}$  to  $18 \text{ ng/m}^3$ , and all concentrations of CPF-O were  $\leq 0.6 \text{ ng/m}^3$ . We identified the highest levels of indoor CPF (4 of 27 samples  $> 9 \text{ ng/m}^3$ ) in proximal and non-proximal farmworker households. Overall, farmworker households had higher indoor air concentrations of CPF than non-farmworker households (Table 3, Kruskal Wallis test,  $p < 0.05$ ).

During the summer, indoor air concentrations of AZM were lower than CPF, ranging from  $< \text{LOD}$  to  $0.8 \text{ ng/m}^3$  (Table 2). For example, 9 of 26 (35%) of indoor air samples yielded detectable levels of AZM, and only 3 of 26 (12%) had detectable levels of AZM-O. There were no significant differences in indoor air concentrations of AZM or AZM-O between farmworker/non-farmworker and proximal/non-proximal households (Table 3). We identified the highest levels of indoor AZM (2 of 26 samples  $> 0.2 \text{ ng/m}^3$ ) in non-proximal farmworker households. All indoor AZM air samples in non-farmworker households were  $< \text{LOD}$ .

### ***Indoor/Outdoor Concentration Ratios***

We present the mean indoor/outdoor ratios by household type in Table 4. All households reported CPF and CPF-O indoor/outdoor ratios less than 1, except for one proximal farmworker

household that reported a CPF indoor/outdoor ratio of 1.3. The overall indoor/outdoor ratio during spring was 0.17 and 0.05 for CPF and CPF-O, respectively. This indicated higher concentrations outdoors as compared to indoors. Farmworker households reported higher indoor/outdoor ratios of CPF than non-farmworker households (Kruskal Wallis test,  $p < 0.001$ ).

Most households reported AZM indoor/outdoor ratios less than 1, except for two non-proximal farmworker households that reported indoor/outdoor ratios of 2.1 and 2.5. The overall indoor/outdoor ratio during the summer was 0.44 and 0.72 for AZM and AZM-O, respectively. Many of the reported ratios for CPF-O and AZM-O included substitute values for measurements below the LOD.

### ***Indoor Surface Deposition***

We present the results of surface deposition by household type in Table 5. Surface deposition measurements for CPF ranged from  $< \text{LOD}$  to  $5.7 \text{ ng/cm}^2$ , and 15 of 27 (55%) of measurements were  $< \text{LOD}$ . Surface deposition measurements for AZM were lower than CPF, ranging from  $< \text{LOD}$  to  $1.6 \text{ ng/cm}^2$ , and 7 of 26 (27%) of surface deposition measurements were  $< \text{LOD}$  for AZM. Overall, proximal households had higher levels of CPF on surfaces than non-proximal households (Table 3, Kruskal Wallis test,  $p < 0.05$ ). We observed very low levels of oxygen analogs in surface deposition samples (all  $\leq 0.3 \text{ ng/cm}^2$ ). We identified the highest deposition levels of CPF (4 of 27 samples  $\geq 1 \text{ ng/cm}^2$ ) at two proximal farmworker and two non-proximal farmworker households. We identified the highest deposition levels of AZM (4 of 26 samples  $\geq 0.5 \text{ ng/cm}^2$ ) at one proximal farmworker and three non-proximal farmworker households. The correlation was stronger for indoor CPF ( $R_s = 0.83$ ,  $p < 0.001$ ) than for AZM

( $R_s = 0.49$ ,  $p < 0.04$ ). We do not report correlations for oxygen analogs due to the large number of samples below the LOD.

### ***Winter Season (Control) Results***

During the winter, outdoor air concentrations of CPF ranged from  $< \text{LOD}$  to  $5.8 \text{ ng/m}^3$ , and CPF-O ranged from  $< \text{LOD}$  to  $0.4 \text{ ng/m}^3$  (Table 2). All air samples for AZM and AZM-O were below the LOD. Two proximal farmworker households had detectable indoor air concentrations of CPF ranging from  $0.02 - 0.9 \text{ ng/m}^3$ ; and all other indoor air samples were below the LOD for CPF-O, AZM, and AZM-O. All indoor surface deposition samples were below the LOD. During the winter, the overall indoor/outdoor ratio for CPF was 0.06.

### **Discussion**

Our study is the first to use simultaneous passive sampling methods to measure outdoor air concentrations, indoor air concentrations, and surface deposition of OP pesticides and their oxygen analogs in a residential setting. The passive methods captured monthly exposure estimates of CPF, CPF-O, AZM, and AZM-O with agreement between replicate samples and relatively low limits of detection when compared to more traditional active air sampling methods (NIOSH 1995, EPA 1999). In addition, the passive methods were minimally invasive to research participants. For example, two participants stated that they “hardly noticed the sampler was there.” There is great potential for the use of more passive sampling methods (such as PUF-PAS) in future epidemiology studies, particularly those being conducted in rural areas with limited outdoor electricity. The PUF-PAS provides good means of comparison because larger numbers of samples can be deployed over time, providing useful information for geographical

information systems. We found the passive devices to be relatively low cost (e.g., the passive matrices were approximately 1% of the overall cost of daily active air sampling matrices required for the same time period). Since the samplers report cumulative exposures over the course of an entire month, researchers no longer need to exclusively rely on producer application reporting. However, there are some limitations to passive sampling. Since passive samplers report monthly averages, it is not possible to specify ‘peak’ exposure days. We have also found that sampling rates are highly influenced by meteorological factors, such as wind velocity (Armstrong et al. 2014a). In this study, we were able to control for such factors by using depuration compounds, since their rate of loss is also affected by temperature and wind velocity (Tuduri et al. 2006).

Overall, we found that outdoor and indoor air concentrations and surface deposition results for CPF and CPF-O during the spring were 5 to 10 times higher than AZM and AZM-O during the summer. We continued to measure low levels of airborne CPF and CPF-O ( $< 6$  ng/m<sup>3</sup>) in a subset ( $k = 6$ ) of locations during the dormant winter season. Since the ban on use of AZM occurred in the year following this study (2012), it is possible that during the summer of 2011 tree fruit producers had already begun to use alternative products. This may have resulted in lower levels of AZM and AZM-O than we expected.

All reported outdoor air concentrations were within the range of concentrations reported in previous studies in California and Washington states (CARB 1999; CDPR 2006, 2009; Fenske et al. 2009). The indoor CPF air concentrations were within or below the range of concentrations reported in a 2004-2005 residential study in New York City conducted by Columbia University (Whyatt et al. 2007). In the present study, the levels of indoor air concentrations of CPF were 0.3-17.5 ng/m<sup>3</sup>, as compared to 0.4-177 ng/m<sup>3</sup> in the Columbia study. However, CPF was used

residentially in New York City for treatment of pests in homes and apartment buildings until 2002. In the present study, CPF was used primarily for outdoor agricultural purposes.

Outdoor air concentrations were higher for households in close proximity to tree fruit fields and households with farmworkers than outdoor concentrations at non-proximal households and non-farmworker households, respectively (Table 3). Proximal households (< 250 m from the nearest tree fruit field) had significantly higher mean outdoor air concentrations of CPF, CPF-O, and AZM ( $p = 0.02$ ,  $0.01$ , and  $< 0.001$ , respectively). Various studies have previously demonstrated associations between proximity and higher residential OP pesticide levels in air, dust, and in biomarkers of near-by residents (Loewenherz et al. 1997, Lu et al. 2000, Fenske et al. 2002). However, we defined “proximal” household by distance (in meters) to only tree fruit fields, and this definition was limited. First, it was unknown if the tree fruit field had been applied with OP pesticides during the sampling period. Second, during the course of the study we learned that the highest levels of CPF air concentrations were measured at 3 proximal farmworker households that within 100 m of corn and wheat fields—in addition to tree fruit fields. In the future, proximity to grain fields should also be considered in geographical regions where corn and grain is more widespread, as CPF is used to control worms, corn borer, and aphid pests in corn and wheat (Gomez, 2009).

We found that air concentrations of CPF were lower indoors as compared to outdoors. The trend was similar for AZM, but it was not statistically significant. Inside the home, very little CPF-O or AZM-O was detected. This was expected, as there is less photolysis (via UV light) to break down parent compounds.

We identified higher indoor air concentrations of CPF in households with close proximity to tree fruit fields ( $p = 0.03$ ) and farmworker status ( $p = 0.01$ ) when compared to households that

non-proximal and did not have farmworkers (Table 3). These findings are similar to other studies that have identified farming households as more contaminated (Simcox et al. 1995; Bradman et al. 1997).

Overall, the indoor/outdoor ratios were lower for CPF than for AZM. During this study, we noted another important factor affecting indoor infiltration. At the end of the study period, the *promotora* asked household members if they remembered opening the windows during the spring, summer, and winter seasons. During the spring season (while sampling for CPF), only 2 of the households indicated opening windows due to colder weather; whereas during the summer season (while sampling for AZM), 10 of the households indicated opening the windows rather than using air conditioning. During the winter season, no households reported opening windows. The open windows may have contributed to the difference in indoor/outdoor ratios by allowing more AZM to come indoors due to higher air exchange rates (Laumbach et al. 2015). Nevertheless, we found that farmworker households reported higher indoor/outdoor ratios for CPF and CPF-O. Therefore, the potential source of indoor pesticides in non-proximal farmworker households may be more attributable to take home pesticide exposure rather than from outdoor infiltration. To test this theory, future studies should include more factors influencing indoor/outdoor ratios, such as open/closed windows, number people living in the home, number and type of farmworkers in the home, and type of air conditioning and heating units.

Although indoor surface depositions of CPF and AZM were higher in proximal households than non-proximal households, there were no statistically significant differences observed between farmworker/non-farmworker household deposition samples (Table 3). There

was good correlation between indoor surface deposition measurements and air concentrations ( $R_s = 0.83$  and  $0.49$  for CPF and AZM, respectively).

There were some limitations to this study. First, we relied on very simple non-parametric statistical test methods rather than multivariable modeling because we were very limited by small sample size. In particular, we found it difficult to identify non-farmworker households that were also proximal since such a large portion of the population is involved in agriculture. Since this was our first attempt to deploy the PUF-PAS samplers for pesticides in a residential setting, we refrained from conducting a larger study in more households. Second, many indoor air and surface deposition samples were below limits of detection, and we had to rely on substituted values for analysis. For future studies using indoor sampling methods for OP pesticides, we suggest using sampling periods of 3-6 months rather than only 1 month. Third, we did not account for the non-independence of replicate samples from the same location and time period, although we deployed replicate samples across all household groups (Supplemental Material, Table S1). Finally, although our ideal sampling period was one month, the sampling periods ranged from 24 to 32 days, since we had to coordinate the deployment schedule with household members. Although there is variation in pesticide use within a season, it was unlikely that this variation contributed to differences in pesticide levels, as there were no significant differences in sampling deployment periods between household groups.

## Conclusions

We demonstrated the use of passive sampling methods for measuring long term (1 month) exposures to OP pesticides and oxygen analogs in a remote agricultural area, and encourage others researchers to explore the use of passive sampling devices (like the PUF-PAS) in their

region. Exposure data is currently lacking for sub-chronic and chronic epidemiological investigations in rural communities.

We have used passive sampling methods to identify higher outdoor and indoor air concentrations and surface deposition of OP pesticides and their oxygen analogs at both proximal (<250 m of a tree fruit field) and farmworker households. This study has further confirmed our previous findings on the presence of OP pesticide oxygen analogs in air. On a residential level, human exposures to these oxygen analogs seem to be a greater concern outdoors than indoors. We have found that both proximal and farmworker households have higher levels of exposure to these airborne compounds. When considering cumulative and aggregate effects of human exposure to OP pesticides, the inclusion of oxygen analogs in future risk assessments will be necessary—especially if spending a large quantities of time outdoors in rural agricultural areas near applied fields. More research is required to describe the community transport of these pesticide mixtures and how oxygen analogs are formed in outdoor environments.

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**Table 1: Chemical properties of CPF, AZM, and suitability for passive sampling with PUF-PAS.** Since there is limited data on oxygen analogs, the analog compound was assumed to have chemical properties similar to the parent compound.

Chemical	Mol. Weight	Log K <sub>ow</sub>	Log K <sub>OA</sub> <sup>a</sup>	solubility (mg/L)	Henry's Constant <sup>b</sup> (atm m <sup>3</sup> /mole)	Vapor Pressure (mmHg) (25 deg C)	Volatility
Chlorpyrifos	350.59	4.27	8.36	0.39	6.76E-01	1.23E-05	Semi-volatile
Azinphos Methyl	317.32	3.38	11.34	14	5.70E-06	3.80E-04	Semi-volatile

Data on chemical properties from PubChem CID 2016, 2268, and 2730.

<sup>a</sup> Log K<sub>OA</sub> (octanol air partition coefficient) is calculated from the Log K<sub>OW</sub> (octanol water partition coefficient) using the ideal gas constant and Henry's Constant value (Meylan and Howard, 2005).

<sup>b</sup> Henry's Constant values great than 10<sup>-8</sup> and Log K<sub>OA</sub> values 7 – 13 indicate that the compound is ideal for passive sampling with PUF.

**Table 2: Summary of outdoor and indoor air concentrations (ng/m<sup>3</sup>).**

	Proximal Farmworker			Proximal Non-Farmworker			Non-Proximal Farmworker			Non-Proximal Non-Farmworker			Total
Outdoor Air	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )
<b>Spring</b>													
CPF	12	0	72 ± 60 <sup>a</sup> (20 – 199)	6	0	31 ± 15 <sup>a</sup> (12 – 44)	9 (7)	0	23 ± 13 <sup>a</sup> (9.2 – 42)	9	0	11 ± 6.2 <sup>a</sup> (9.7 – 19)	36 (23)
CPF-O	(7)	0	10 ± 5.5 <sup>a</sup> (3.0 – 20)	(2)	0	4.5 ± 4.2 <sup>a</sup> (2.7 – 15)		0	3.2 ± 3.1 <sup>a</sup> (0.03 – 7.9)	(7)	0	2.5 ± 1.5 <sup>a</sup> (2.2 – 4.3)	
<b>Summer</b>													
AZM	9	0	2.4 ± 2.6 <sup>a</sup> (0.4 – 7.3)	4	0	1.2 ± 0.4 <sup>a</sup> (0.7 – 1.6)	8 (7)	0	0.3 ± 0.1 <sup>a</sup> (0.1 – 0.7)	9	1	0.3 ± 0.2 <sup>a</sup> (< LOD – 0.6)	30 (23)
AZM-O	(7)	4	0.1 ± 0.3 < LOD – 0.8	(2)	2	0.03 ± 0.1 (< LOD – 0.1)		8 <sup>b</sup>	< LOD NA	(7)	6 <sup>b</sup>	0.02 ± 0.03 (< LOD – 0.05)	
<b>Winter<sup>c</sup></b>													
CPF		0	3.5 ± 2.7 (0.6 – 5.8)		1	< LOD (NA)		1	0.3 ± 0.4 (< LOD – 0.6)		1	< LOD (NA)	7 (6)
CPF-O		0	0.2 ± 0.2 (0.02 – 0.4)		1	< LOD (NA)		1	0.02 ± 0.01 (< LOD – 0.02)		1	< LOD (NA)	
AZM	3		< LOD (NA)	1	1	< LOD (NA)	2 (2)		< LOD (NA)	1	1	< LOD (NA)	
AZM-O	(2)	3 <sup>b</sup>	< LOD (NA)	(1)	1	< LOD (NA)		2	< LOD (NA)	(1)	1	< LOD (NA)	
<b>Indoor Air</b>													
<b>Spring</b>													
CPF	8	1	7.9 ± 6.8 (< LOD – 18)	4	1	0.5 ± 0.4 (< LOD – 0.8)	8 (7)	2	3.5 ± 3.8 (< LOD – 9.2)	7	2	0.6 ± 1.8 (< LOD – 0.6)	27 (20)
CPF-O	(6)	5 <sup>b</sup>	0.03 ± 0.1 (< LOD – 0.6)	(2)	3 <sup>b</sup>	0.01 ± 0.01 (< LOD – 0.01)		6 <sup>b</sup>	0.01 ± 0.1 (< LOD – 0.2)	(5)	6 <sup>b</sup>	0.1 ± 0.2 (< LOD – 0.1)	
<b>Summer</b>													
AZM	8	3	0.1 ± 0.1 (< LOD – 0.2)	3	3 <sup>b</sup>	< LOD (NA)	7 (7)	3	0.3 ± 0.2 (< LOD – 0.8)	8	8 <sup>b</sup>	< LOD (NA)	26 (20)
AZM-O	(6)	6 <sup>b</sup>	0.10 ± 0.04 (< LOD – 0.3)	(2)	3 <sup>b</sup>	< LOD (NA)		6	0.02 ± 0.3 (< LOD – 0.06)	(5)	8 <sup>b</sup>	< LOD (NA)	
<b>Winter<sup>c</sup></b>													
CPF	3	0	0.2 ± 0.5 (0.02 – 0.9)	1	1	< LOD (NA)	2 (2)	2	< LOD (NA)	1	1	< LOD (NA)	7 (6)
CPF-O	(2)	3 <sup>b</sup>	< LOD (NA)	(1)	1	< LOD (NA)		2	< LOD (NA)	(1)	1	< LOD (NA)	

AZM	3	< LOD (NA)	< LOD (NA)	2	< LOD (NA)	1	< LOD (NA)
AZM-O	3	< LOD (NA)	< LOD (NA)	2	< LOD (NA)	1	< LOD (NA)

Abbreviations:  $n$  = number of samples;  $k$  = number of locations; LOD = limit of detection; NA = Not available;  $n < \text{LOD}$  = number of samples  $<$  LOD; Std = standard deviation

<sup>a</sup>  $p < 0.1$  for differences across all household types (2-way Friedman's Test)

<sup>b</sup> Count ( $n < \text{LOD}$ ) includes replicate samples that were  $< \text{LOD}$ .

<sup>c</sup> Winter was a dormant season, therefore a limited number of samples were collected.

**Table 3: Comparisons between proximal vs. non-proximal and farmworker vs. non-farmworker for outdoor air concentrations (ng/m<sup>3</sup>), indoor air concentrations (ng/m<sup>3</sup>), and surface deposition (ng/cm<sup>2</sup>). We did not compare winter samples due to limited sample size.**

Outdoor Air (ng/m <sup>3</sup> )	Proximal		Non-Proximal		P-value <sup>a</sup>	Farmworker		Non-Farmworker		P-value <sup>a</sup>
	n	Mean ± Std	n	Mean ± Std		n	Mean ± Std	n	Mean ± Std	
<b>Spring</b>										
CPF	18	53.4 ± 53.9	18	18.2 ± 10.1	0.02	21	48.2 (50.9)	15	17.7 (10.4)	0.01
CPF-O		7.5 ± 4.3		3.1 ± 2.3	0.01		5.8 (4.3)		4.6 (3.6)	0.01
<b>Summer</b>										
AZM	13	2.1 ± 2.2	17	0.3 ± 0.2	<0.001	17	1.4 (2.1)	13	0.65 (0.5)	0.18
AZM-O		0.2 ± 0.3		0.02 ± 0.02*	0.69		0.1 (0.2)		0.03 (0.03)*	0.48
<b>Indoor Air (ng/m<sup>3</sup>)</b>										
<b>Spring</b>										
CPF		6.3 ± 5.9		1.4 ± 3.0	0.03		5.4 (5.5)		0.2 (0.3)	0.01
CPF-O	12	0.1 ± 0.2 <sup>b</sup>	17	0.02 ± 0.1 <sup>b</sup>	0.96	16	0.1 (0.2) <sup>b</sup>	11	0.01 (0.0) <sup>b</sup>	0.20
<b>Summer</b>										
AZM	11	0.04 ± 0.1 <sup>b</sup>	15	0.1 ± 0.2) <sup>b</sup>	0.82	15	0.1 (0.2) <sup>b</sup>	11	0.03 (0.1) <sup>b</sup>	0.12
AZM-O		0.03 ± 0.1 <sup>b</sup>		0.01 ± 0.01 <sup>b</sup>	NA		0.03 (0.1) <sup>b</sup>		< LOD	NA
<b>Indoor Surface (ng/cm<sup>2</sup>)</b>										
<b>Spring</b>										
CPF		1.2 ± 2.2 <sup>b</sup>		0.2 ± 0.5 <sup>b</sup>	0.01		1.0 (1.9) <sup>b</sup>		0.1 (0.1) <sup>b</sup>	0.37
CPF-O	12	0.06 ± 0.1 <sup>b</sup>	15	0.01 ± 0.05 <sup>b</sup>	NA	16	0.06 (0.1) <sup>b</sup>	11	< LOD	NA
<b>Summer</b>										

<b>AZM</b>										
	11	0.3 ± 0.5 <sup>b</sup>	15	0.2 (0.2) <sup>b</sup>	0.03	16	0.4 (0.4) <sup>b</sup>	10	0.04 (0.05) <sup>b</sup>	0.09
<b>AZM-O</b>		0.01 ± 0.01 <sup>b</sup>		< LOD	NA		< LOD		< LOD	NA

Abbreviations: *n* = number of samples; LOD = limit of detection; NA = Not available

<sup>a</sup> *p* < 0.05 for differences between groups (Kruskal-Wallis test)

<sup>b</sup> The calculated mean and standard deviations include substituted values < LOD and may not reflect the true value.

**Table 4: Indoor/outdoor air concentration ratios by household type.** Indoor/outdoor ratios were calculated individually for each household. The mean ratios were then calculated by proximal farmworker, proximal non-farmworker, non-proximal farmworker, and non-proximal non-farmworker households.

	Proximal Farmworker		Proximal Non-Farmworker		Non-Proximal Farmworker		Non-Proximal Non-Farmworker		Overall	
Spring	<i>k</i>	I/O ratio (Mean)	<i>k</i>	I/O ratio (Mean)	<i>k</i>	I/O ratio (Mean)	<i>k</i>	I/O ratio (Mean)	<i>k</i>	I/O ratio (Mean)
CPF		0.29		0.01		0.49		0.005		0.17
CPF-O	6	0.03 <sup>a</sup>	2	0.002 <sup>a</sup>	7	0.11 <sup>a</sup>	5	0.004 <sup>a</sup>	20	0.05
Summer										
AZM		0.13		0.80 <sup>a</sup>		0.77		0.24 <sup>a</sup>		0.44
AZM-O	6	0.48 <sup>a</sup>	2	0.67 <sup>a</sup>	7	0.79 <sup>a</sup>	5	0.72 <sup>a</sup>	20	0.72
Winter										
CPF <sup>b</sup>	2	0.06	1	< LOD (NA)	2	< LOD (NA)	1	< LOD (NA)	6	< LOD (NA)

Abbreviations: *k* = number of locations; I/O = Indoor/Outdoor Ratio, a ratio greater than 1 indicates higher indoor pesticide concentrations, and a ratio less than 1 indicates higher outdoor pesticide concentrations. LOD = limit of detection; NA = Not available

<sup>a</sup> These results were calculated using more than 50% substituted values < LOD, therefore they may over or under estimate the true ratio.

<sup>b</sup> All other indoor air samples were below the LOD for CPF-O, AZM, and AZM-O, so ratios could not be calculated.

**Table 5: Summary of indoor surface deposition (ng/cm<sup>2</sup>).**

	Proximal Farmworker			Proximal Non-Farmworker			Non-Proximal Farmworker			Non-Proximal Non-Farmworker			Total
	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )	<i>n</i> < LOD	Mean ± Std (min, max)	<i>n</i> ( <i>k</i> )
<b>Spring</b>													
CPF	8 (6)	2	1.7 ± 2.6 (< LOD – 5.7)	4 (2)	2	0.2 ± 0.1 (< LOD – 0.3)	8 (7)	6	0.3 ± 0.6 (< LOD – 1.4)	7 (5)	5	0.1 ± 0.1 (< LOD – 0.3)	27 (20)
CPF-O		3	0.1 ± 0.1 (< LOD – 0.3)		4	< LOD (NA)		6	0.03 ± 0.1 (< LOD – 0.2)		7	< LOD (NA)	
<b>Summer</b>													
AZM	8 (6)	2	0.5 ± 0.6 (< LOD – 1.6)	3 (2)	1	0.1 ± 0.1 (< LOD – 0.1)	8 (7)	1	0.3 ± 0.3 (< LOD – 0.7)	7 (5)	3	0.04 ± 0.04 (< LOD – 0.1)	26 (20)
AZM-O		4	0.04 ± 0.1 (< LOD – 0.1)		3	< LOD (NA)		8	< LOD (NA)		7	< LOD (NA)	
<b>Winter<sup>a</sup></b>													
	3 (2)	3	< LOD (NA)	1(1)	1	< LOD (NA)	2 (2)	2	< LOD	1 (1)	1	< LOD (NA)	7 (6)

Abbreviations: *n* = number of samples; *k* = number of locations; LOD = limit of detection; NA = Not available; *n* < LOD = number of samples < LOD

<sup>a</sup> Winter was a dormant season, therefore a limited number of samples were collected.

**Figure 1. Map of Yakima Valley, Washington State study region.**

**Figure 2. Sampling time-line.** Sampling occurred in 2011 during the spring application season for CPF and CPF-O, summer application season for AZM and AZM-O, and in the winter dormant season for CPF, CPF-O, AZM, and AZM-O.

Figure 1.



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Figure 2.

